Physica B 463 (2015) 76–81

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Letter to the Editor

Effect of multi-walled carbon nanotubes aspect ratio and temperature on the dielectric behavior of alternating alkene-carbon monoxide polyketone nanocomposites

ARTICLE INFO

Keywords:
Polyketone
Nanocomposite
Impedance
Conductivity
Permittivity
Modulus

ABSTRACT

New alternating poly(propylene-*alt*-carbon monoxide/ethylene-*alt*-carbon monoxide) (PECO)/multi-walled carbon nanotubes (MWCNTs) composites have been prepared. Dielectric permittivity, electric modulus and ac conductivity of the isolated materials were investigated as a function of fiber aspect ratio, frequency and temperature. For aspect ratio of 30 and 200, a transition from insulator to semi-conductor was observed at frequency 1×10^4. However, for high aspect ratio sample (660), no transition was observed and the conductivity is frequency independent in the measured frequency range of 10–10^6 Hz. The conductivity increases from about 1×10^{-4} for the sample that contain fibers of aspect ratio 30 and reaches 5×10^{-2} $(\Omega\,m)^{-1}$ for aspect ratio was 660. This behavior can be modeled by a circuit that consists of a contact resistance in series with a parallel combination of resistance (R) and capacitance (C). The calculated activation energy for sample filled with fibers having aspect ratio 30 is about 0.26 eV and decreases to about 0.16 eV when the aspect ratio is 660.

1. Introduction

Traditional fibers, made from inorganic substances, such as alumina or glass were used as fillers in composites. Compared to those fibers, carbon nanotubes (CNTs) showed many superior properties such as low-weight, very high aspect ratio, high electrical conductivity, and much higher fracture strain [1]. These incomparable properties of CNTs make them desirable materials for fabrication of advanced nanocomposites with variable features.

Numerous applications of polymer/CNTs composites where reported include electromagnetic shielding [2] electronic components [3], nonlinear optics [4] and solar energy materials [5]. The named composites may have the capability to replace conventional inorganic semiconductors [6–8]. It is important to note that upon using high aspect ratio, the composite will attain the percolation limit at lower fillers concentration and a jump in conductivity will be observed [9–12].

Many polymer/nanofiller composites combinations have been studied in literature. Different nanofillers (single and multiwalled carbon nanotubes) have been used. The polymer matrices studied ranged from conventional polymers such as polyethylene [13], polypropylene [14,15], and polystyrene [16], to high performance polymers such as polycarbonate [17,18] and polyetherketone [19,20]. Beyond the threshold concentration, the nanofillers can create conductive networks in the insulating matrix that results in a dramatic increase in the conductivity of the composite by different folds [21–28]. For industrial applications of polymer/CNT composites, it is desirable to achieve the percolation limit with the least content of fillers. In order to attain this limit, the conductive network in the polymer matrix should be formed which can be achieved using high aspect ratio.

Perfectly alternating polyketones have useful chemical and physical properties in terms of photodegradability, biodegradability, chemical resistance, and ease of functionalization [29,30]. Furthermore, polymer properties such as crystallinity, stereochemistry, molecular weight, polarity, mechanical properties and thermal behavior can easily be tuned by the right choice of the monomer(s) and their ratio [31,32], type of catalyst [33–35], and reaction conditions [36]. For example, excellent elastic properties were obtained when the molar ratio of ethylene-carbon monoxide (E-CO) segments to the propylene-carbon monoxide (P-CO) in the terpolymer chain was less than 50%. When this ratio was increased above 50%, a typical crystalline thermoplastic was obtained [36,37].

Recently, we reported the electric impedance of the alternating propylene, ethylene and carbon monoxide co- and terpolymers as a function of frequency and temperature [38,39]. The results for the propylene-*alt*-carbon monoxide copolymer (PCO) revealed a phase transition at about 70 °C. At this temperature the material transforms from insulating to conductive phase where its conductivity increased from 6×10^{-9} to about 9×10^{-5} $(\Omega\,m)^{-1}$. However, the dielectric behavior of the crystalline ethylene-*alt*-CO/propylene-*alt*-CO terpolymer shows two distinct regions. The first region, which falls below the first transition temperature, is characterized a weak dependence of the ac- and dc-conductivities on temperature and frequency. In the second region, which falls above the first transition temperature, the electric modulus reveals the relaxation process which was masked at the intermediate frequency in the plot of the dielectric loss.

In addition, the dielectric properties, ac conductivity and charge transport mechanisms in propylene-alt-CO/ethylene-alt-CO random terpolymer filled with multi-walled carbon nanotubes (MWCNTs) as a function of nanofiller content, frequency, and temperature were investigated. Equivalent resistor-capacitor (RC)

http://dx.doi.org/10.1016/j.physb.2015.01.039
0921-4526/© 2015 Published by Elsevier B.V.

circuit models were proposed to describe the impedance characteristics of the unfilled terpolymer and the nanocomposite at different temperatures. For the nanocomposites, the ac conductivity tended to be frequency independent at low frequencies [40] and increases with increasing frequency follows the power law behavior [41].

In the present work, we report on the control of the electric properties of elastomeric nanocomposites by using MWCNTs with different aspect ratio. The new materials were prepared from propylene-*alt*-carbon monoxide/ethylene-*alt*-carbon monoxide terpolymer and MWCNTs with different diameters (10–20 and 40–60 nm) and fiber lengths (1–2 and 5–15 μm). The dielectric permittivity and ac conductivity were calculated from impedance measurements at different temperatures.

2. Experimental

2.1. Materials and method

The alternating terpolymer, propylene-*alt*-carbon monoxide/ethylene-*alt*-carbon monoxide ($Mw=1.9\times10^5$, $Mw/Mn=2.4$), with 48% ethylene-CO units, was prepared via coordination polymerization following a previously published procedure [35,42] (Fig. 1). The multi-walled carbon-nanotubes were obtained from Shenzhen Nanotech Port Co., Ltd., purity ≥ 95%, (Table 1).

2.2. Preparation of the polyketone-multi-walled carbon-nanotubes composites (B1, B2 and B3).

Three nano-composites filled with 5 wt% MWCNs (Table 1) were prepared by adding the corresponding MWCNs to 0.5 g of the polymer in 20 ml methylene chloride. The mixture was gently mixed for 20 min using a sonicator. The solvent was then removed by slow evaporation at room temperature, in order to keep the aspect ratio in MWCNTs (length/diameter) intact. The nanocomposites (B1, B2 and B3) were isolated as thin films.

2.3. Impedance measurements

AC impedance measurements were performed in the frequency range between 10 and 10^6 Hz and temperature range from 20 °C to 100 °C. The experiments were conducted using a Solartron-1260 Impedance/Gain Phase Analyzer with a 1294 dielectric interface. Two software packages, Z-60 and Z-View, were used to maximize the performance and data handling of the system. By measuring the amplitude and the phase shift of the resulting current, one can calculate the real and imaginary components of the complex impedance. The real and imaginary components of dielectric constant, and ac conductivity were determined and plotted as a function of frequency at different temperatures.

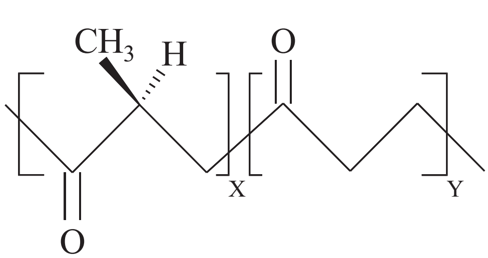

Fig. 1. Chemical structure of the terpolymer: propylene-*alt*-carbon monoxide/*ethylene-alt*-carbon monoxide.

Table 1
Types of multi-walled carbon-nanotubes (MWNTs) used in the present study.

Code	Length (μm)	Main range of diameter (nm)	Aspect ratio
B1	5–15	10–20	660
B2	5–15	40–60	200
B3	1–2	40–60	30

2.4. Scanning electron microscopy

A Hitachi S-2700 scanning electron microscope equipped with a Princeton gamma tech (PGA) IMIX digital imaging system was used to examine the dispersion of nanotubes in the composites. SEM images were performed at Nano Technology Center at Jordan University of Science and Technology.

3. Results and discussion

Fig. 2(a), (b) and (c) depicts selected SEM images of composite samples B1, B2 and B3 respectively. The images indicate that MWCNTs are well dispersed in the polymer matrix. Since the nanotubes are wavy and entangled, the evaluation of their dimensions in the composite was not possible. Saleh and Sundaraj [42] reported that the reduction in fiber length after sonication varies from 19% to 38% depending on the sonication time. Consequently, due to wide range in the apparent aspect ratio (30 up to 660) of our samples, and the mixture was gently mixed for 20 min, our expectation is that the variations in the actual aspect ratio remains significant after sonication process. Therefore, the reported results on the dielectric behavior were assigned to the effect of aspect ratio.

To study the effect of aspect ratio and temperatures on the dielectric behavior of MWCNTs fiber/polyketone composite, we report our results in terms of imaginary (Z'') and real (Z') parts of complex impedance, dielectric loss (ε''), ac conductivity and electric modulus. Fig. 3 shows the variation of normalized (Z') and (Z'') versus frequency at 20 °C for B1, B2 and B3 samples. The same features of the impedance spectra was observed for B2 and B3 samples. The impedance spectra for B2 and B3 samples can be modeled by a circuit consisting of a contact resistance R_s in series with a parallel combination of R_p and C (Fig. 3).

For this circuit the complex impedance can be written as

$$Z_* = Z' - iZ'' = R_s + \frac{R_p}{1 + i\omega\tau} \quad (1)$$

where $\tau=RC$, from the above equation the real Z' and imaginary parts of the complex impedance can be written as

$$Z' - R_s = \frac{R_p}{1 + (\omega\tau)^2} \quad \text{and} \quad Z'' = \frac{\omega\tau R_p}{1 + (\omega\tau)^2} \quad (2)$$

The plot of Z' versus Z'' satisfy the following relation:

$$\left[Z' - R_s - \frac{R_p}{2}\right]^2 + Z''^2 = \left(\frac{R_p}{2}\right)^2 \quad (3)$$

The plot of Z' versus Z'' yields a semicircle having its center at $R = ((R_s + R_p)/2), 0$, with a diameter$=R_p$.

The proposed model for B2 and B3 samples gives the values of the contact resistance, (R_s) about 140 Ω and R_p as 18,473, and 27,543 Ω for B2 and B3 respectively. The results give a value R_p exactly the same as the value of the real part of impedance in the plateau region where Z' is independent of frequency. The frequency independent region extends to higher frequencies with increasing fiber aspect ratio to cover all the measured frequency